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## **JAPANESE / ENGLISH TRANSLATION OF**

**Japanese Patent Application JP 53 – 90233 A**

**Title: Method for the Purification of Terephthalic Acid**

**Your Ref: No. 9140**

**For: Eastman Chemical Company -  
Library and Information Services (LibriS)**

(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application  
(Kokai) No.

(12) Unexamined Patent Gazette (A)

**53-90233**

(51) Int. Cl. <sup>2</sup>	Classification Symbols	(52) Japanese Classification	Internal Office Registration Nos.	(43) Date of Publication: August 8, 1978
C 07 C 63/26		16 C 61	6652-43	
C 07 C 51/44		16 C 619	6652-43	

Request for Examination: Not yet submitted

Number of Inventions: 1

Total of 5 pages [in original]

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(54) Title of the Invention: **Method for the Purification of Terephthalic Acid**

(21) Application No.: 52-2324

(22) Date of Filing: January 14, 1977

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## SPECIFICATION

### 1. Title of the Invention

Method for the Purification of Terephthalic Acid

### 2. Claims

A method for the purification of terephthalic acid, wherein terephthalic acid obtained as a result of oxidizing p-xylene with a gas containing molecular oxygen in an aliphatic carboxylic acid solvent in the presence of a catalyst is subjected to a multistage treatment in a purification medium of which the principal component is water or acetic acid, said method characterized in

that at least one stage of the multistage treatment includes a treatment at 140°C or higher, and the separation filtrate of a subsequent stage is circulated and used as the purification medium of a prior stage.

### **3. Detailed Description of the Invention**

The present invention relates to a method for the purification of terephthalic acid. In particular, it provides a purification method for providing a level of quality that can be used in the manufacture of polyethylene terephthalate with the help of a method in which terephthalic acid that contains a comparatively large amount of impurities and has been manufactured by means of the liquid-phase oxidation of p-xylene with a gas containing molecular oxygen is subjected to so-called direct polymerization.

Because of the difficulty of purifying terephthalic acid as a principal component, conventional methods for manufacturing polyethylene terephthalate on a commercial scale entail purifying terephthalic acid by means of converting it to a dimethyl ester, recrystallizing the ester, distilling the product, and the like, whereupon ester interchange with a glycol is performed to form bis-( $\beta$ -hydroxyethyl) terephthalate, and the terephthalate is polycondensed to obtain the target polyethylene terephthalate.

However, in recent years, with the advances in the purification of terephthalic acid, the so-called direct polymerization method, in which polyethylene terephthalate is manufactured directly without being converted to a dimethyl ester, has come into use on a commercial scale.

It is necessary that the quality of the terephthalic acid used for direct polymerization be at a higher level than that considered for ordinary chemical products. If the terephthalic acid is not of so-called fiber-grade quality, coloration and other effects undesirable in terms of polymer quality are known to occur when the product is used in direct polymerization.

Known methods for obtaining high-quality terephthalic acid include a method in which crude terephthalic acid is purified as a result of being heated, dissolved in a solvent such as acetic acid, and recrystallized (recrystallization treatment, JP (Kokoku) 33-8184), as well as a method in which terephthalic acid is made into a slurry with a purification medium such as acetic acid, and

some or most of the terephthalic acid contained is purified as a result of being heated in a state in which the acid is present in the solid state (suspension treatment, JP (Kokoku) 44-13135). It is known that the degree of purity can be increased in response to performing these treatments individually, combining the two treatments, or performing the treatments over several stages.

Although a high degree of quality can be achieved as a result of using the terephthalic acid obtained by means of these direct polymerization methods, it is still difficult to regard this approach as sufficient. Accordingly, the inventors conducted intensive studies on whether there is a method for further purification of terephthalic acid that would be more economical and advantageous. As the result, they arrived at this invention.

Specifically, this invention is a method for purification of terephthalic acid wherein terephthalic acid obtained as a result of oxidizing p-xylene with a gas containing molecular oxygen in an aliphatic carboxylic acid solvent in the presence of a catalyst is subjected to a multistage treatment in a purification medium of which the principal component is water or acetic acid, the method characterized in that at least one stage of the multistage treatment includes a treatment at 140°C or higher, and the separation filtrate of a subsequent stage is circulated and used as the purification medium of a prior stage.

The crude terephthalic acid to be purified according to this invention should be terephthalic acid that is obtained as a result of the liquid-phase oxidation of p-xylene with a gas containing molecular oxygen in a lower carboxylic acid solvent and in the presence of a catalyst. For example, crude terephthalic acid obtained by means of a method in which p-xylene is oxidized with a bromine compound as the reaction promoter can be used. However, terephthalic acid that is obtained as a result of the so-called low temperature oxidation method in which the acid is manufactured under comparatively mild conditions is more suitable.

Acetic acid is used as the principal reaction solvent. A reaction promoter may or may not be used. When it is used, known acetaldehyde, methyl ethyl ketone, paraldehyde, or a bromine compound can be selected.

The oxidation reaction may be performed with the help of the continuous method or the batch method. The reaction temperature should be 80 to 250°C. The crude terephthalic acid that

is obtained in this way is separated from the reaction mixture. The acid is then dried or made into a wet cake without drying, and is fed to the prescribed purification system of this invention. A centrifuge is ordinarily used to separate the terephthalic acid.

The principal component of the purification system is water or acetic acid, with an aqueous solution of acetic acid ordinarily being used. Multistage treatment means a treatment in two or more stages.

The first characteristic of this invention is that at least one stage of the multistage treatment includes a treatment at 140°C or higher. In short, it is necessary that a process performed at least at 140°C or higher be present at some point in the total purification treatment process. When the entire treatment is performed at less than 140°C, the purity of the terephthalic acid is not sufficiently increased.

The second characteristic of this invention is that, in this multistage treatment process, a subsequent separation filtrate is circulated and used as the purification medium of a prior stage. For example, when the total treatment process consists of three stages, the separation filtrate used in the treatment in the second stage is circulated and used as the purification medium (treatment solution) of the first stage, and the separation filtrate used in the treatment in the third stage is used in the treatment of the second stage. In this case, after the purification treatment of each stage, separation is ordinarily performed using a separating device, so the fine terephthalic acid particles and the filtrate can be completely separated by means of adjusting the separation efficiency, and any desired quantity of terephthalic acid particles can be present on the filtrate side. When the inventors treated terephthalic acid with a purifying medium in this way, they discovered that larger quantities of impurities were present as the particle diameters of the terephthalic acid decreased. Consequently, a desirable mode of this invention is a method in which separation is performed after each stage (more precisely, after the second stage) without completely separating the solid and liquid when the terephthalic acid particles and the purification medium are separated, that is, in a state in which terephthalic acid particles containing a large amount of impurities are present in a smaller quantity on the filtrate side, and the separation filtrate is then circulated and used as the purification medium of the prior stage.

As a result of sequentially cutting off small particles containing large amounts of impurities in each separation stage in this way, terephthalic acid of extremely high purity can be obtained.

We shall now describe the purification process of this invention by reference to Figure 1. Figure 1 shows the second of the several treatment stages of this invention.

Crude terephthalic acid that has been manufactured as described previously is supplied via a line 1 to a first mixing tank 2. The separation filtrate of the second stage is supplied via a line 18 to the first mixing tank 2 as the purification medium and is mixed with the terephthalic acid. The principal component of this separation filtrate is water or acetic acid. It may also contain byproducts of the oxidation reaction, unreacted material, methyl acetate, formic acid, and p-xylene. As described subsequently, the separation filtrate may also contain some minute particles of terephthalic acid.

The proportion of terephthalic acid and medium in the first mixing tank 2 should be 1:1 to 1:20 (weight ratio).

This terephthalic acid mixture is supplied via a line 3 to a first heat treatment apparatus 4, and a specified heat treatment is performed.

The heat treatment may be an ordinary recrystallization procedure for purification in which the terephthalic acid is dissolved in the purification medium at a high temperature and high pressure, after which it is recrystallized, or it may also be a heat treatment performed in a state of suspension in which some or most of the terephthalic acid is present as a solid in the purification medium. However, it is necessary that the heat treatment temperature be 140°C or higher, and, preferably, 150°C or higher, in at least one stage of the first stage and the second stage.

Although there are no particular limitations on the heat treatment time, it is ordinarily 0.1 to 10 hours.

After the heat treatment, the terephthalic acid mixture is cooled with the help of a suitable cooling method. The mixture is then supplied via a line 5 to a first separator 6 and is recovered as a terephthalic acid wet cake, which is supplied via a line 7 to a second-stage mixing tank 8.

The cooling method can be an ordinary method in which cooling is effected as a result of the latent heat of evaporation of steam produced by means of decreasing pressure, a method in which cooling is effected indirectly from the outside through a heat exchanger, or a method in which cooling is effected by means of the direct introduction of a cooling medium.

In the first stage separator 6, classification and removal of small particles is not particularly necessary, and the separation efficiency is set to a level at which there is no admixture and loss of terephthalic acid with the separation filtrate.

Because the separation filtrate of the first stage separator contains a large amount of impurities, the solvent is usually evaporated from an evaporator 10 and is purified by means of separating some of the terephthalic acid and impurities as nonvolatile components. The product is fed to the second-stage mixing tank 8 as a clear purification medium.

The terephthalic acid wet cake that has been recovered in the first separator 6 is mixed in the mixing tank 8 with the purification medium via a line 11, and is fed to a second-stage heat treatment apparatus 13 via a line 12. The principal component of the purification medium that passes through the line 11 is also water or acetic acid, and is purified in the evaporator, but may still contain byproducts of the oxidation reaction and unreacted materials such as, for example, methyl acetate, formic acid, and p-xylene.

The second-stage heat treatment, like the first stage, may be an ordinary heated solvent recrystallization treatment or it may be a heat treatment in a state of suspension.

It is not necessary for the first stage and second stage to be the same heat treatment, and there may be a combination in which the first stage is a suspension heat treatment and the second stage is a solution recrystallization, or it may be the converse of this. Of course, the first stage and second stage may also involve performing the same heat treatment.

However, when first stage is performed at a temperature less than 140°C, it is necessary that the second stage be performed at a temperature greater than 140°C.

A terephthalic acid mixture that has been subjected to the second-stage heat treatment is appropriately cooled in the same manner as in the first stage and is then fed to a second separator 15 through a line 14.

In the second separator 15, the clarity of the separation filtrate decreases somewhat, and small particles containing a large amount of impurities are contained in the separation filtrate. The filtrate is passed through the line 18 and may be used again as the first-stage (prior stage) purification medium.

The proportion in which terephthalic acid is fed to the separator is determined by the impurity content of small particles, which should be moved to the separation filtrate or removed. In general, removing large amounts of small particles increases the quality of the product, but adopting this approach increases the amount of terephthalic acid that circulates through the apparatus and requires a bulkier apparatus with the same treatment capacity.

Ordinarily, the removal ratio of small particles should be 0.5 to 25 wt%, and, preferably, 1 to 10 wt%, relative to the total weight of terephthalic acid that is fed to the separator. That is, terephthalic acid particles of this range are preferably contained in the filtrate and recycled.

An ordinary centrifuge can be used as the separator. Removal of small particles is achieved as a result of adjusting the separation efficiency (degree of filtrate clearness) of the separator.

Figure 1 shows an example in which the heat treatment of an embodiment of this invention is divided into two stages. However, terephthalic acid of higher quality can be manufactured as a result of increasing the embodiment to three or four stages.

We shall now describe this invention in specific terms by means of working examples.

### **Working Example 1**

Crude terephthalic acid was obtained as a result of the liquid phase air oxidation of p-xylene at a temperature of 120°C and a pressure of 20 kg/cm<sup>2</sup> G in acetic acid (solvent) using cobalt acetate as the solvent and paraldehyde as the reaction promoter.



The crude terephthalic acid that was obtained contained 3000 ppm of p-formylbenzoic acid as an impurity. A wet cake containing 200 parts by weight of this crude terephthalic acid was mixed without drying with 1200 parts by weight of second-stage separation filtrate in the first mixing tank (2) of the purification flow shown in Figure 1, and a mixed slurry was obtained. The principal components contained in the 1200 parts by weight of the second-stage separation filtrate were 1040 parts by weight of acetic acid, 150 parts by weight of water, and some methyl acetate and p-xylene. At this time, the second-stage separation filtrate did not contain any solid terephthalic acid particles and was completely clear.

The mixed slurry described above was subjected to a suspension heat treatment for one hour at a temperature of 130°C and a pressure of 9 kg/cm<sup>2</sup> G, after which the pressure was reduced from 9 kg/cm<sup>2</sup> G to 0 kg/cm<sup>2</sup> G, and the mixed slurry was cooled from 130°C to 105°C by way of its latent heat of evaporation.

After cooling, the mixed slurry and the filtrate were separated in the first stage centrifuge (6), and a wet cake containing 200 parts by weight of terephthalic acid was obtained.

The separation filtrate in the first stage separator was evaporated in the evaporator, and some of the acetic acid was added to the concentrated solution to make 1200 parts by weight of a second-stage purification medium.

This purification medium and the terephthalic acid wet cake were mixed, a second-stage suspension heat treatment was performed at 150°C and 9 kg/cm<sup>2</sup> G, and the materials were cooled as in the first stage, after which the filtrate and the wet cake were separated in the second-stage centrifuge (15), and drying was performed with a dryer. As the result, the quantity of terephthalic acid obtained was 198 parts by weight.

At this time, separation efficiency was adjusted so that there were no solid terephthalic acid particles in the second-stage separation filtrate.

After drying, there was 1270 ppm of p-formylbenzoic acid in the terephthalic acid that was obtained, and the yield of terephthalic acid in the purification process was 99%.

## **Working Example 2**

A wet cake containing 200 parts by weight of crude terephthalic acid obtained under the same reaction conditions as described in Working Example 1 was mixed without drying with 1200 parts by weight of the second-stage separation filtrate in the purification flow shown in Figure 1, and a mixed slurry was obtained.

There were 1040 parts by weight of acetic acid, 150 parts by weight of water, 8 parts by weight of small particles of solid terephthalic acid, and some methyl acetate and p-xylene in the 1200 parts by weight of the second-stage separation filtrate.

The mixed slurry was subjected to a second-stage suspension heat treatment in the same way as described in Working Example 1. The slurry was then cooled and subjected to second stage separation. The resulting wet cake was dried, and 198 parts by weight of terephthalic acid was obtained.

At this time, the separation efficiency was adjusted so that the second-stage separation filtrate contained 8 parts by weight of solid terephthalic acid particles. This corresponded to 3.9 wt% relative to 206 parts by weight of the terephthalic acid fed to the second-stage separator.

After drying, there was 1000 ppm of p-formylbenzoic acid in the terephthalic acid that was obtained, and the yield of terephthalic acid in the purification process was 99%.

## **Comparative Example 1**

When the procedures were carried out as described in Working Example 2, except that the second-stage separation filtrate was not used as a second-stage purification medium, and the purification medium that had been evaporated and concentrated in the evaporator was used instead, there was 990 ppm p-formylbenzoic acid in the terephthalic acid that was obtained, and the yield of terephthalic acid in the purification process was reduced to 95%.

At this time, the separation efficiency was adjusted so that there was 8 parts by weight of solid terephthalic acid particles in the second-stage separation filtrate. This corresponded to 4.0 wt% relative to 198 parts of the terephthalic acid fed to the second-stage separator.

## Comparative Example 2

When the procedure was performed in the same way as in Comparative Example 1, except that the second-stage heat treatment temperature was set to 130°C in the same manner as in the first stage, there was 1400 ppm of p-formylbenzoic acid in the terephthalic acid that was obtained, and the yield of terephthalic acid in the purification process was 95%.

On the other hand, when the procedure was performed in the same way as described in Working Example 2, except that the second-stage heat treatment temperature was set to 130°C, the yield of terephthalic acid in the purification process was increased to 99%. However, the content of p-formylbenzoic acid in the terephthalic acid that was obtained was increased to 1700 ppm, purification efficiency was markedly reduced, and it was concluded that the effect of the present invention was not manifested.

## 4. Brief Description of the Drawings

Figure 1 is a flow diagram that shows an embodiment of this invention. The numerals and letters in the figure are indicated below.

- 1, 3, 5, 7, 9, 11, 12, 14, 16, and 18: pipes
- 2: first mixing tank
- 4: first heat treatment apparatus
- 6: first separator
- 8: second mixing tank
- 10: evaporator
- 13: second-stage heat treatment apparatus
- 17: drier
- A: first-stage treatment
- B: second-stage treatment

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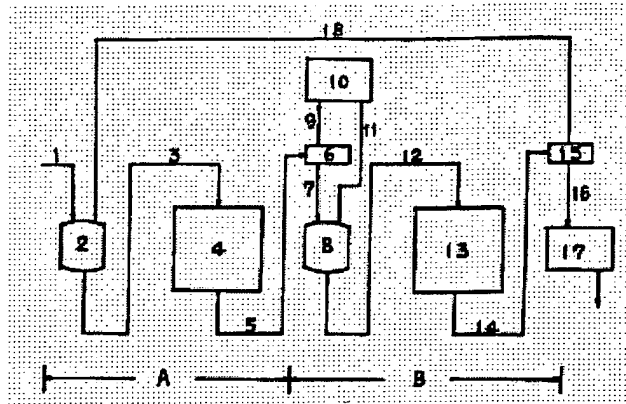


Figure 1